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Phase transformations in metastable liquids combined with polymerization

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This paper is concerned with the theory of nucleation and growth of crystals in a metastable polymer melt with allowance for the polymerization of a monomer. A mathematical model consisting of the heat balance equation, equations governing the particle-radius distribution function and the polymerization degree is formulated. The exact steady-state analytical solutions are found. In the case of unsteady-state crystallization with polymerization, the particle-size distribution function is determined analytically for different space–time regions by means of the Laplace transform. Two functional integro-differential equations governing the dimensionless temperature and polymerization degree are deduced. These equations are solved by means of the saddle-point technique for the evaluation of a Laplace-type integral. The time-dependent distribution function, temperature and polymerization degree at different polymerization rates and nucleation kinetics are derived with allowance for the main contribution to the Laplace-type integral. In addition, the general analytical solution by means of the saddle-point technique and an example showing how to construct the analytical solutions in particular cases are given in the appendices. The analytical method developed in the present paper can be used to describe the similar phase transition phenomena in the presence of chemical reactions.

This article is part of the theme issue 'Heterogeneous materials: metastable and non-ergodic internal structures'.

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1. Introduction

The dynamics of many metastable systems is often controlled not only by the rate of particle nucleation and the kinetics of their growth but also by chemical reactions that radically affect the processes of heat and mass transfer. Examples of such processes include the simultaneous occurrence of polymerization phenomenon and bulk crystallization in continuous apparatuses, biochemical processes of origination, evolution, and death of microorganisms, and the like. Mathematical models of such processes are described by nonlinear integro-differential equations with moving boundaries of structural and phase transformations. Since there are no general methods for solving such problems, the solution of each individual problem requires the development of new original approaches.

One of the successful approaches that make it possible to construct an analytical solution of the integro-differential model of nucleation and growth of crystals in the absence of polymerization is the theory developed in papers [1–4]. In these papers, a method for solving integral equations is developed on the basis of the saddle-point technique for evaluating the Laplace-type integrals. By using this approach, it is possible to determine the dynamics of desupercooling (desupersaturation) of a metastable system and the evolution of the crystal size distribution function. This method also makes it possible to construct a solution of a more complicated problem that takes into account the removal of crystals from the crystallizer, and also the heat sink or mass source [5]. This approach can be extended to investigate polymerization phenomena that differ from pure crystallization by the physical mechanism of the process. From the point of view of the mathematical model, the closest process to bulk crystallization is the emulsion polymerization phenomenon, which is studied at the modelling level of the dynamics of polymer particles. This allows us to use previously developed methods for solving the integro-differential bulk crystallization model for describing the emulsion polymerization. Note that the kinetics of polymerization of emulsions was previously investigated by a number of authors (see, among others, [6–8]). So, for example, the process of emulsion polymerization of vinyl chloride was investigated by Heiskanen [8] on the basis of evolutionary momentum equations.

An important circumstance is the fact that within a certain temperature range the process of nucleation and growth of crystallites from a metastable polymer liquid occurs simultaneously with the polymerization process [9–12]. Note that in many cases the latent heat of crystallization is comparable with the heat of polymerization [9]. In such processes, the effect of polymerization can become decisive. This is enhanced by the development of instabilities and the formation of new wave regimes associated with the polymerization phenomenon [13–16].

In this paper, we consider the dynamic phenomenon of anionic polymerization, which occurs synchronously with the process of bulk crystallization. An important point is that the theory under consideration is valid for arbitrary kinetic mechanisms of crystallization and polymerization. The method of solving the nonlinear problem of combined crystallization and polymerization developed below is based on the construction of a general functional solution of the kinetic equation for the crystal size distribution function. The balance equations then allow us to obtain the integro-differential equations for the polymerization degree and relative temperature, which are solved using the saddle-point method. The analytical theory developed in this work can be used to describe the process of bulk crystallization occurring in the presence of chemical reactions of a different nature.

The manuscript is organized as follows. Section 2 is devoted to the formulation of a mathematical model governing the combined process of crystallization and polymerization in a metastable liquid. This integro-differential system of kinetic and balance equations is solved in §3 on the basis of the Laplace transform and saddle-point methods. The dynamical behaviour of our solutions is illustrated and discussed in §4. In §5, we present our final remarks and conclusions.

2. The model of combined crystallization and polymerization

Let us discuss some physical assumptions concerning the process under consideration. The paper deals with the phenomenon of polymerization in a monomer metastable melt, simultaneously

with the process of crystallization of the evolving polymer. We will also consider an ideally mixed metastable system. This means that the physico-chemical properties of the system are assumed to be homogeneous throughout the metastable melt volume. In practice, this state of the system can be obtained by means of intensive mixing of the liquid in a crystallizer [17]. Such a hypothesis makes it possible to substantially simplify the formulation of the problem, namely, to consider many physical coefficients independent of spatial coordinates. Also, we consider such an idealized polymerization process, when the formed polymer does not swell after its origination. The process of phase transformation is considered at its intermediate stage. In other words, we do not consider such phenomena as Ostwald ripening, coagulation, and disintegration of evolving aggregates, which take place at the final stage of the phase transformation. We also assume that the growing crystals have a spherical shape. In this case, the size distribution of the crystals can be described using a single spatial parameter, the radius of the crystal. In a more general case, when there is no spherical symmetry of the problem, it is necessary to use more parameters to describe the distribution function of growing aggregates [18].

Let us introduce the current temperature T of a metastable medium and the polymerization degree w, which determines the polymerized fraction of the monomer to its total mass. The evolutionary behaviour of these process parameters is described by the following balance equations:

$$\rho c \frac{\mathrm{d}T}{\mathrm{d}t} = \alpha\,(T_m - T) + \rho_1 L_1 H(w,T) + \rho_2 L_2 \int_{r_*}^{\infty} \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{4\pi r^3}{3}\right) f(r,t)\,\mathrm{d}r, \quad t > 0 \tag{2.1}$$

and

$$\frac{\mathrm{d}w}{\mathrm{d}t} = H(w,T) - g_* w, \quad t > 0, \tag{2.2}$$

where ρ and c are the density and specific heat of mixture, α is the effective heat transfer coefficient, T_m is the temperature of external consumer, ρ_1 and L_1 are the density of polymer and latent heat of polymerization, H is the polymerization rate, ρ_2 and L_2 are the density of crystals and latent heat of crystallization, r_* is the critical radius of crystals, r and t are the spatial and time variables and g_* is the withdrawal rate of melt. Note that the critical radius r_* determines the critical size of the nucleating crystals, which are capable of further growth. Let us especially emphasize that the first term in the right-hand side of equation (2.1) is caused by the linear law of heat exchange between the crystallizer and the external environment.

The particle-radius distribution function $f(r,t)$ obeys the kinetic equation

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial r}\left(\frac{\mathrm{d}r}{\mathrm{d}t} f\right) + g(r) f = 0, \quad t > 0,\ r > r_*, \tag{2.3}$$

where $g(r)$ represents the crystal withdrawal rate (this function is inversely proportional to the mean waiting time of crystals of size r in the crystallizer).

The flux of crystals overcoming the critical barrier and capable of further growth is determined by the nucleation rate $J(w,T)$. Taking this into account, we have the boundary condition

$$\frac{\mathrm{d}r}{\mathrm{d}t} f = J(w,T), \quad r = r_*,\ t > 0. \tag{2.4}$$

Note that the nucleation rate represents an exponential function

$$J(w,T) = J_0 \exp\left[\lambda \varphi(w,T)\right] \tag{2.5}$$

in the case of the Weber–Volmer–Frenkel–Zel'dovich nucleation kinetics, where J_0 is the pre-exponential factor, λ is the dimensionless Gibbs number and φ is a function of w and T (φ is determined in [2] when considering crystallization without polymerization).

It is important to note that the polymerization rate H represents a nonlinear function of temperature T and polymerization degree w. The non-stationary solution of the problem constructed below is valid in the case of an arbitrary dependence $H(w,T)$. As one of the possible

dependencies $H(w,T)$, let us write down the following power law with respect to the substrates

$$H(w,T) = H_0\,(1-w)^n \exp\left(-\frac{E}{k_B T}\right), \tag{2.6}$$

where H_0 and n are the model constants, E is the energy and k_B is the Boltzmann constant.

Let us express the growth velocity of polymeric crystals as a product of two functions dependent on r and T in the form [9,19–22]

$$\frac{\mathrm{d}r}{\mathrm{d}t} = F(r)B(T). \tag{2.7}$$

Note that the rate of crystal growth is often independent of their radius r (see, among others, [23–25]).

The initial conditions to equations (2.1)–(2.3) can be written as

$$T(0) = T_i, \quad w(0) = w_i, \quad f(r,0) = f_i(r), \quad t = 0, \tag{2.8}$$

where the subscript i denotes the initial values.

The system of equations, boundary and initial conditions (2.1)–(2.8) represents a closed model for investigating the dynamics of the process of bulk crystallization combined with polymerization. The general method for solving the formulated integro-differential model is developed in the next section. This method is applicable for describing the nucleation and growth of a new phase with allowance for polymerization in the case of arbitrary dependencies for the nucleation rate $J(w,T)$, polymerization rate $H(w,T)$ and crystal growth rate (2.7). In addition, the method developed below can be applied to the theoretical description of the nucleation and growth of crystals in metastable systems in the presence of other chemical reactions.

3. Stationary and non-stationary analytical solutions

The formulated problem can be conveniently solved using the following dimensionless variables:

$$\left.\begin{aligned}
&t_* = g_* \int_0^t \frac{B\,[u(\tau)]}{B_s}\,\mathrm{d}\tau, \quad s = g_* \int_0^r \frac{\mathrm{d}r_1}{F\,(r_1)\,B_s},\\
&h\,(s,t_*) = \ln\left[f\,(r,t)\,F(r)\right], \quad G(s) = \frac{g(r)}{g_*},\\
&u = \frac{T_0 - T}{T_0}, \quad K = \frac{\rho_1 L_1 w_s}{\rho c T_0 u_s}, \quad \sigma = \frac{\alpha\,(u_m - u_s)}{\rho c g_* u_s},\\
&\sigma_m = \frac{\alpha u_m}{\rho c g_* u_s}, \quad u_m = \frac{T_0 - T_m}{T_0}, \quad h_i\,(s) = \ln\left[f_i\,(r)\,F(r)\right]\\
&\text{and} \qquad X = \int_0^\infty \exp\left[-\int_0^s G(z)\,\mathrm{d}z\right] r^2(s) F(s)\,\mathrm{d}s.
\end{aligned}\right\} \tag{3.1}$$

For simplicity, we neglect the critical radius of the crystals, i.e. $r_* = 0$.

The problem (2.1)–(2.8) in dimensionless variables (3.1) takes the form

$$\begin{aligned}
&\frac{B(u)}{B_s}\frac{\mathrm{d}}{\mathrm{d}t_*}\left(\frac{u}{u_s} + K\frac{w}{w_s}\right) + (\sigma_m - \sigma)\left(\frac{u}{u_s} - 1\right) + K\frac{w}{w_s} - \sigma\\
&\quad + \frac{(\sigma - K)\,B(u)}{J_s X}\int_0^\infty f\,(s,t_*)\,r^2(s)F^2(s)\,\mathrm{d}s = 0,
\end{aligned} \tag{3.2}$$

$$\frac{B(u)}{B_s w_s}\frac{\mathrm{d}w}{\mathrm{d}t_*}+\frac{w}{w_s}=\frac{H\left[w\left(t_*\right),u\left(t_*\right)\right]}{H_s}, \tag{3.3}$$

$$\frac{\partial h}{\partial t_*}+\frac{\partial h}{\partial s}+\frac{B_s G(s)}{B\left[u\left(t_*\right)\right]}=0, \tag{3.4}$$

$$h\left(0,t_*\right)=\ln\left\{\frac{J\left[w\left(t_*\right),u\left(t_*\right)\right]}{B\left[u\left(t_*\right)\right]}\right\},\quad h(s,0)=h_i(s) \tag{3.5}$$

and

$$u(0)=u_i=\frac{T_0-T_i}{T_0},\quad w(0)=w_i. \tag{3.6}$$

Here, the subscript s designates the steady-state values.

We first determine the stationary solutions of the system (3.2)–(3.6). In this case, equation (3.4) and the boundary condition (3.5) become

$$\frac{\mathrm{d}h_s(s)}{\mathrm{d}s}=-G(s),\quad h_s(0)=\ln\left(\frac{J_s}{B_s}\right), \tag{3.7}$$

where $B_s=B(u_s)$, $J_s=J(w_s,u_s)$ and $u_s=(T_0-T_s)/T_0$. The boundary-value problem (3.7) leads to the following steady-state distribution function

$$f_s(s)=\frac{\exp\left[h_s(s)\right]}{F(s)}=\frac{J_s}{F(s)B_s}\exp\left[-\int_0^s G(z)\,\mathrm{d}z\right]. \tag{3.8}$$

Now combining expressions (3.2), (3.3) and (3.8) in the steady-state conditions, we obtain

$$H\left(w_s,u_s\right)=g_* w_s=H_s,\quad \sigma-K=\frac{4\pi\rho_2 L_2 J_s B_s X}{T_0 g_*^2 \rho c u_s}. \tag{3.9}$$

Note that equations (3.9) determine the stationary polymerization degree w_s and the stationary relative temperature u_s.

Let us now consider the transient regime of crystal growth and polymerization. Applying the Laplace transform to equation (3.4) with respect to the spatial variable s and taking into account the boundary and initial conditions (3.5), we get

$$\frac{\mathrm{d}h_p}{\mathrm{d}t_*}+ph_p-\ln\left\{\frac{J\left[w\left(t_*\right),u\left(t_*\right)\right]}{B\left[u\left(t_*\right)\right]}\right\}+\frac{B_s G_p}{B\left[u\left(t_*\right)\right]}=0,\quad h_p(0)=h_{ip}, \tag{3.10}$$

where subscript p designates the Laplace transform, and p is the Laplace transform variable. The analytical solution of the boundary-value problem (3.10) takes the form

$$h_p(t_*)=h_{ip}\exp\left(-pt_*\right)+\int_0^{t_*}\left\{\ln\frac{J\left[w\left(t_1\right),u\left(t_1\right)\right]}{B\left[u\left(t_1\right)\right]}-\frac{B_s G_p}{B\left[u\left(t_1\right)\right]}\right\}\exp\left[-p\left(t_*-t_1\right)\right]\mathrm{d}t_1. \tag{3.11}$$

Keeping in mind the inverse Laplace transforms

$$\exp\left(-pa\right)\to\delta\left(s-a\right),\quad f_{1p}f_{2p}\to\int_0^s f_1\left(\bar{s}\right)f_2\left(s-\bar{s}\right)\,\mathrm{d}\bar{s}$$

and the property of Delta function

$$\int_{-\infty}^{\infty}f(x)\delta(x-y)\,\mathrm{d}x=f(y),$$

we come to the following non-stationary distribution function

$$f\left(s,t_*\right)=\begin{cases}\dfrac{f_i\left(s-t_*\right)F\left(s-t_*\right)}{F(s)}\exp\left\{-B_s\displaystyle\int_0^{t_*}\frac{G\left(s-t_*+x\right)\,\mathrm{d}x}{B\left[u(x)\right]}\right\}, & s\geq t_*,\\ \dfrac{J\left[w\left(t_*-s\right),u\left(t_*-s\right)\right]}{F(s)B\left[u\left(t_*-s\right)\right]}\exp\left\{-B_s\displaystyle\int_{t_*-s}^{t_*}\frac{G\left(s-t_*+x\right)\,\mathrm{d}x}{B\left[u(x)\right]}\right\}, & s<t_*.\end{cases} \tag{3.12}$$

Note that the distribution functions (3.12) coincide at $s=t_*$.

Let us now rewrite the growth rate of crystals (2.7) in dimensionless form as

$$\frac{\mathrm{d}s}{\mathrm{d}t_*} = 1, \tag{3.13}$$

or after integration

$$s = t_* - \nu, \tag{3.14}$$

where $s = 0$ at $t_* = \nu$. In other words, the growth rate (3.14) at $\nu = 0$ describes the radius s_m of nuclei that appeared at the initial time. An important point is that if a metastable liquid did not initially contain any crystals ($f_i(s) = 0$), which nucleate and grow at $t_* > 0$, the distribution function (3.12) is determined at $s < t_*$ only. In other words, it is described by the second line of expression (3.12). On the other hand, if the initial distribution function $f_i(s) \neq 0$ (a metastable system initially contains the crystals), the situation changes drastically. If this is really the case, we have newly born crystals corresponding to the second line of the distribution function (3.12) as well as the initially existing crystals that evolve with time according to the first line of the distribution function (3.12). In any case, the relative temperature u and polymerization degree w can be found by means of substitution of the distribution function (3.12) into the balance equation (3.2). After this substitution, we must solve two differential equations (3.2) and (3.3). However, the integral term entering into equation (3.2) can be evaluated analytically on the basis of the saddle-point technique for a Laplace-type integral in the case when a metastable liquid did not initially contain any crystals. We describe this case below to simplify the model equations for $u(t_*)$ and $w(t_*)$.

Now substituting the distribution function (3.12) into the heat balance equation (3.2) and changing the variable s of integration at any fixed t_* by the new variable ν in accordance with (3.14), we arrive at

$$\frac{B(u)}{B_s}\frac{\mathrm{d}}{\mathrm{d}t_*}\left(\frac{u}{u_s} + K\frac{w}{w_s}\right) + (\sigma_m - \sigma)\left(\frac{u}{u_s} - 1\right) + K\frac{w}{w_s} - \sigma + \frac{(\sigma - K)\,B(u)}{J_s X}\int_0^{t_*} J\left[w(\nu), u(\nu)\right]\Theta\,(\nu, t_*)\;\mathrm{d}\nu = 0 \tag{3.15}$$

and

$$\Theta\,(\nu, t_*) = \frac{r^2(t_* - \nu)F(t_* - \nu)}{B\left[u\,(\nu)\right]}\exp\left[-B_s\int_\nu^{t_*}\frac{G(x - \nu)\,\mathrm{d}x}{B\left[u\,(x)\right]}\right].$$

Here, we took into account that $\mathrm{d}s = -\mathrm{d}\nu$ and the limits of integration $s = 0$ and $s = s_m$ transform to the corresponding limits $\nu = t_*$ and $\nu = 0$.

Now substituting the nucleation rate from expression (2.5) into the right-hand side of the thermal balance condition (3.15), one can evaluate the integral contribution by the saddle-point method. Keeping in mind that the nucleation rate J decreases as time increases, the exponent $\varphi(\nu) = \varphi[w(\nu), u(\nu)]$ is a decreasing function too. It means that $\mathrm{d}\varphi/\mathrm{d}\nu < 0$ and the maximum value of the function $\varphi(\nu)$ attains at the boundary $\nu = 0$. Taking this into account and keeping in mind only the main contribution of the saddle-point method [26], we get

$$\int_0^{t_*} J_0 \exp\left\{\lambda\varphi\left[w(\nu), u(\nu)\right]\right\}\Theta\,(\nu, t_*)\;\mathrm{d}\nu \approx -\frac{J_0\Theta\,(0, t_*)\exp\left[\lambda\varphi\,(w_i, u_i)\right]}{\lambda\varphi'(0)}. \tag{3.16}$$

Here, we assume that $\varphi'(0) \neq 0$ (a more general case is considered in appendix A).

Substituting (3.16) into (3.15), we have

$$\frac{B(u)}{B_s}\frac{\mathrm{d}}{\mathrm{d}t_*}\left(\frac{u}{u_s} + K\frac{w}{w_s}\right) + (\sigma_m - \sigma)\left(\frac{u}{u_s} - 1\right) + K\frac{w}{w_s} - \sigma - \frac{(\sigma - K)\,B(u)J_0\Theta\,(0, t_*)\exp\left[\lambda\varphi\,(w_i, u_i)\right]}{J_s X\lambda\varphi'(0)} = 0. \tag{3.17}$$

Now the first-order differential equations (3.3) and (3.17) together with the initial conditions (3.6) completely determine the evolutionary behaviour of the polymerization degree $w(t_*)$ and

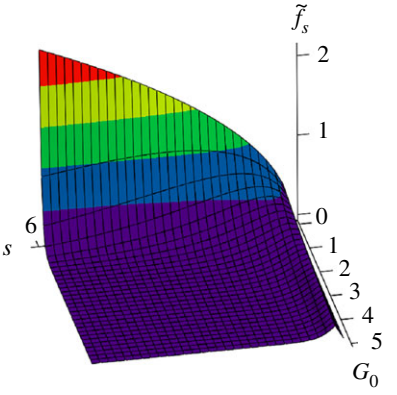

Figure 1. The steady-state distribution function $\tilde{f}(s, G_0)$ shown according to expression (B 5).

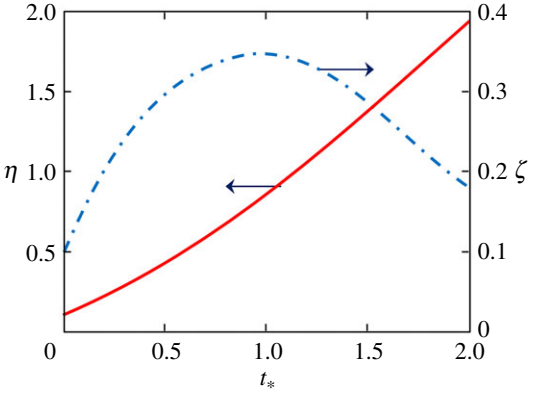

Figure 2. The dimensionless temperature η and polymerization degree ζ versus dimensionless time t_*. Parameters used in calculations are: $B_s/B_0 = 1$, $K = 2$, $H_0/H_s = 2$, $n = 1$, $u_s = 0.5$, $w_s = 0.2$, $\tilde{E} = 1$, $\sigma_m = 2$, $\sigma = 1.5$, $\eta_i = 0.1$, $\zeta_i = 0.1$, $\tilde{A} = 0.01$ and $\lambda = 2$. (Online version in colour.)

the relative temperature $u(t_*)$. Note that this system of nonlinear equations can be easily solved numerically.

4. Nonlinear behaviour of solutions

Appendix B is devoted to the question of how to calculate the analytical solutions (3.3), (3.12) and (3.17) in a simple particular case. Here, we use the analytical dependencies (B 1)–(B 5) derived there.

Figure 1 demonstrates the steady-state particle-size distribution function $\tilde{f}_s$ versus the radius s of particles and relative crystal withdrawal rate G_0. At any fixed value G_0, the distribution function represents a bell-shaped curve. This function also decreases with increasing G_0. As one can see, the crystal withdrawal rate is one of the main system parameters, which controls the stationary distribution function in a metastable liquid.

Figure 2 shows the analytical solution of the Cauchy problem (B 1)–(B 3) for the determination of a transient behaviour of the relative temperature η (or u) and polymerization degree ζ (or w). It is easily seen that the dimensionless temperature increases with time. This is due to the fact that the metastability degree reduces with time as a result of the release of latent heat by the growing crystals, which in part compensates for the supercooling. The polymerization degree initially increases because the polymerization rate exceeds the withdrawal rate of melt at small

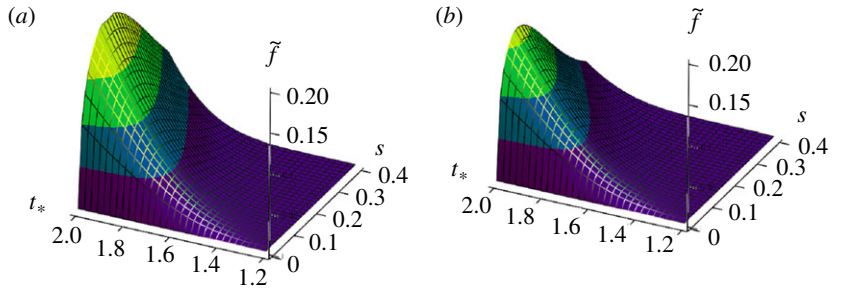

Figure 3. The unsteady-state distribution function $\tilde{f}(s, t_*) = f(s, t_*)/\Sigma$ shown according to expression (B 4) at different dimensionless crystal withdrawal rates: $G_0 = 1$ (*a*) and $G_0 = 3$ (*b*).

times. When the melt withdrawal rate becomes greater, the polymerization degree becomes a decreasing function of time. The maximum point is described by the steady-state equation (2.2) or (3.3).

The time-dependent distribution function of particles with allowance for their polymerization is illustrated in figure 3 according to the analytical solution (B 4). Note that this solution is determined at $s < t_*$ (see, for details, the second line in expression (3.12)). As we might expect, the distribution function is a bell-shaped curve at a fixed time. This function increases with time as crystals nucleate and grow. In addition, the distribution function decreases as the relative crystal withdrawal rate G_0 increases (compare figure 3*a*,*b*).

5. Conclusion

In this paper, a new analytical method for solving problems regarding the bulk phase transition in a metastable liquid is developed, taking into account the polymerization effect. The theory is constructed for the intermediate stage of a phase transformation phenomenon with allowance for such nonlinear processes as the heat exchange of the reactor with an external consumer, the withdrawal rates of a polymer melt and crystals, and the nucleation-polymerization kinetics. The analytical method developed in this paper can be used to describe structural and phase transitions in other physical systems, such as granulation, coalescence and coagulation phenomena, heterogeneous or homogeneous mist formation in a supercooled air, combustion of dispersed fuels and the like. When considering different industrial applications of the aforementioned processes, an important question arises about the stability of solutions. Therefore, the dynamical and/or morphological stability analysis should be carried out in the spirit of works [27–30]. Such a theory represents a challenging problem for future investigations in different applications of the phase transformation phenomena.

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Competing interests. The authors declare that they have no competing interests.

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Appendix A. The saddle-point technique

Let us write out the general approximation of the integral term (3.15) according to the saddle-point method [26]

$$\int_0^{t_*} J_0 \exp\{\lambda\varphi[w(\nu), u(\nu)]\}\, \Theta(\nu, t_*)\, \mathrm{d}\nu \approx J_0 \lambda^{-1/m} \exp[\lambda\varphi(w_i, u_i)] \sum_{k=0}^{\infty} a_k \lambda^{-k/m}, \tag{A 1}$$

where m determines the order of the first non-zero derivative at $\nu = 0$, i.e.

$$\varphi'(0) = \cdots = \varphi^{(m-1)}(0) = 0, \quad \varphi^{(m)}(0) \neq 0,$$

$$a_k = \frac{(-1)^{k+1} m^k}{k!} \Gamma\left(\frac{k+1}{m}\right) \left[q(\nu) \frac{\mathrm{d}}{\mathrm{d}\nu}\right]^k \left[\Theta(\nu, t_*)\, q(\nu)\right], \quad \nu = 0$$

and

$$q(\nu) = \frac{\{\varphi[w(\nu), u(\nu)] - \varphi[w_i, u_i]\}^{1-1/m}}{\varphi'(\nu)}.$$

In this case, equation (3.15) becomes

$$\frac{B(u)}{B_s} \frac{\mathrm{d}}{\mathrm{d}t_*} \left(\frac{u}{u_s} + K \frac{w}{w_s}\right) + (\sigma_m - \sigma) \left(\frac{u}{u_s} - 1\right) + K \frac{w}{w_s} - \sigma + \frac{(\sigma - K)\, B(u) J_0 \lambda^{-1/m}}{J_s X} \exp\left[\lambda \varphi(w_i, u_i)\right] \sum_{k=0}^{\infty} a_k \lambda^{-k/m} = 0. \tag{A 2}$$

Thus, differential equations (3.3) and (A 2) together with the initial conditions (3.6) describe the evolutionary behaviour of the polymerization degree $w(t_*)$ and the relative temperature $u(t_*)$ in a more general case at arbitrary functions $\varphi(w, u)$, $H(w, u)$, $G(s)$, $F(s)$ and $B(u)$.

Appendix B. An example showing how to construct the analytical solutions

This section is concerned with the evaluation of the relative temperature and polymerization degree dynamics as well as the particle-size distribution function in accordance with the analytical solutions (3.3), (3.12) and (3.17). Let us consider a simple case of crystal growth with polymerization taking into account the following expressions $G(z) = G_0 = \text{const}$, $B(u) = B_0 = \text{const}$ and $F(r) = F_0/r$, where subscript 0 denotes the constant values. Substituting these dependencies into (3.1), we have

$$r(s) = \sqrt{\frac{2F_0 B_s s}{g_*}}, \quad F(s) = F_0 \sqrt{\frac{g_*}{2F_0 B_s s}}, \quad X = \frac{2F_0 \kappa}{G_0^{3/2}} \sqrt{\frac{2F_0 B_s}{g_*}},$$

$$\kappa = \int_0^{\infty} y^2 \exp\left(-y^2\right) \mathrm{d}y \approx 0.44$$

and

$$\Theta(\nu, t_*) = \frac{F_0}{B_0} \sqrt{\frac{2F_0 B_s (t_* - \nu)}{g_*}} \exp\left[-\frac{B_s G_0 (t_* - \nu)}{B_0}\right].$$

Substitution of these expressions into (3.3) and (3.17) gives the following system of differential equations for the determination of dimensionless temperature $\eta(t_*) = u(t_*)/u_s$ and polymerization degree $\zeta(t_*) = w(t_*)/w_s$

$$\frac{\mathrm{d}\eta}{\mathrm{d}t_*} + \frac{B_s}{B_0} \left[K \frac{H(\zeta, \eta)}{H_s} + (\sigma_m - \sigma)(\eta - 1) - \sigma - \frac{\bar{A}(t_*)}{(\mathrm{d}\eta/\mathrm{d}t_*)_0}\right] = 0 \tag{B 1}$$

and

$$\frac{\mathrm{d}\zeta}{\mathrm{d}t_*} + \frac{B_s}{B_0} \left[\zeta - \frac{H(\zeta, \eta)}{H_s}\right] = 0, \tag{B 2}$$

where $(\mathrm{d}\eta/\mathrm{d}t_*)_0 = \mathrm{d}\eta/\mathrm{d}t_*$ at $t_* = 0$ and

$$\bar{A}(t_*) = \tilde{A} \sqrt{t_*} \exp\left(-\frac{B_s G_0 t_*}{B_0}\right), \quad \tilde{A} = \frac{(\sigma - K) J_0 G_0^{3/2} u_i^3 \exp\left[\lambda\left(1 - u_i^{-2}\right)\right]}{4\lambda\kappa J_s u_s}$$

and

$$H(\zeta, \eta) = H_0 (1 - w_s \zeta)^n \exp\left[-\frac{\tilde{E}}{1 - u_s \eta}\right], \quad \tilde{E} = \frac{E}{k_B T_0}.$$

Note that the derivative $(\mathrm{d}\eta/\mathrm{d}t_*)_0$ can be found from the same equation (B 1). The initial conditions to equations (B 1) and (B 2) follow from conditions (3.6) and take the form

$$\eta = \eta_i = \frac{u_i}{u_s}, \quad \zeta = \zeta_i = \frac{w_i}{w_s}, \quad t_* = 0. \tag{B 3}$$

The problem (B 1)–(B 3) represents the Cauchy problem, which enables us to find the time-dependent behaviour $\eta(t_*)$ and $\zeta(t_*)$.

The crystal-size distribution function follows from the second line (3.12) in the form

$$f(s,t_*) = \Sigma\sqrt{s}\exp\left[-\frac{B_s G_0 s}{B_0}\right]\exp\left[\lambda\left(1-\frac{1}{u_s^2\eta^2\,(t_*-s)}\right)\right], \quad \Sigma = \frac{J_0}{B_0}\sqrt{\frac{2B_s}{g_* F_0}}, \tag{B 4}$$

where, for the sake of definiteness, the Weber–Volmer–Frenkel–Zel'dovich kinetics $\varphi = 1 - u^{-2}$ is taken into account.

Let us also write out an explicit form of the steady-state distribution function (3.8) shown in figure 1.

$$\tilde{f}\,(s,G_0) = \frac{\sqrt{B_s F_0 g_*} f_s(s)}{\sqrt{2}J_s} = \sqrt{s}\exp\left(G_0 s\right). \tag{B 5}$$

The evolutionary behaviour of the present analytical solutions (B 1)–(B 5) is illustrated and analysed in §4.

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